

Structure Factor and Electronic Structure of Compressed Liquid Rubidium

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Abstract

We have applied the quantal hypernetted-chain equations in combination with the Rosenfeld bridge-functional to calculate the atomic and the electronic structure of compressed liquid-rubidium under high pressure (0.2, 2.5, 3.9, and 6.1 GPa); the calculated structure factors are in good agreement with experimental results measured by Tsuji *et al.* along the melting curve. We found that the Rb-pseudoatom remains under these high pressures almost unchanged with respect to the pseudoatom at room pressure; thus, the effective ion-ion interaction is practically the same for all pressure-values. We observe that all structure factors calculated for this pressure-variation coincide almost into a single curve if wavenumbers are scaled in units of the Wigner-

Seitz radius a although no corresponding scaling feature is observed in the effective ion-ion interaction. This scaling property of the structure factors signifies that the compression in liquid-rubidium is uniform with increasing pressure; in absolute Q -values this means that the first peak-position (Q_1) of the structure factor increases proportionally to $V^{-1/3}$ (V being the specific volume per ion), as was experimentally observed by Tsuji *et al.* This scaling property comes from a specific feature characteristic for effective ion-ion potential of liquid rubidium: even if the effective liquid-rubidium potential is invariant under this pressure-variation with respect to the potential at room pressure, we can nevertheless observe this scaling property for the structure factors. This property is obviously characteristic for the potential of alkali metals and we have examined and confirmed this feature for the case of a liquid-lithium potential: starting from the liquid-lithium potential at room pressure we can easily find two sets of densities and temperatures for which the structure factors become practically identical, when scaling Q in units of a .

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I. INTRODUCTION

Based on density-functional (DF) theory, we have derived in previous work a set of integral equations, which allows to calculate the ion-ion and the electron-ion correlations in a liquid metal or a plasma, consistent with the bound-electron structure of the ion using only the atomic number Z_A as input; these integral equations are named the quantal hypernetted-chain (QHNC) equations,^{1,2} which are derived from the exact expressions for the ion-ion and electron-ion radial distribution functions (RDF) in an electron-ion mixture. Up to now, we have applied this approach to liquid metallic hydrogen,¹ lithium,³ sodium,⁴ potassium⁵ and aluminum⁶ obtaining ion-ion structure factors in excellent agreement with experiments. Since a liquid metal can be considered as a very special type of a high-density plasma, we can expect from the successful application of the QHNC-method to liquid metals, that this approach is able to provide accurate results for a plasma. In such a system, both the ionic valency Z_I and the electron-ion interaction $v_{eI}(r)$ may vary over a wide range as temperature and density are changed. Our method is in particular suited to treat a plasma, since it is able to calculate the ionization Z_I and the electron-ion interaction in a self-consistent manner using the atomic number of the system as the only input data.

Recently, we have extended this formalism and have performed a first-principles molecular dynamics (MD) simulation based on the QHNC theory for alkali metals near the triple point: in this study those small deviations which were still observed between experimental results and QHNC data for the structure factor disappeared completely.⁷ Nevertheless, the calculation of the ion-ion RDF in an MD simulation is rather time-consuming. Recently, Rosenfeld⁸ has proposed a new bridge-functional for hard-spheres; its construction requires only fundamental measures of the hard-spheres. In combination with the MHNC-approach – by replacing the *bridge-function* by a *bridge-functional* of the reference system – it was found out that this method is able to give very accurate results for the structure and thermodynamics of a large variety of one-component and binary liquid systems.⁹ Therefore, with replacement of the MD simulations by the MHNC method we can obtain accurate results

for the ion-ion and electron-ion RDF's for dense fluids via the QHNC method using the Rosenfeld bridge-functional.

In a plasma, density and temperature vary over a wide range. Therefore, in order to check the applicability of the approach presented here to a strongly coupled plasma (where no reliable experimental data for particle-correlations are available), it is important to examine to what extent the QHNC equations can describe a liquid metal in a wide range of densities and temperatures. Recently, Tsuji *et al.*¹⁰ measured the structure factors of liquid Rb at high pressures: 0.2, 2.5, 3.9 and 6.1 GPa. These pressure-values bring along a compression of liquid Rb: the corresponding density values are estimated to be 1.07, 1.41, 1.56 and 1.95 times the normal density, respectively.¹¹ Tsuji *et al.* observed that liquid Rb is uniformly compressed with increasing pressure. In this context it should be mentioned that Shimojo *et al.*¹² performed first-principles molecular-dynamics simulation for liquid Rb under pressure (0, 2.5, and 6.1 GPa) and compared their results with the RDF's extracted from the structure factors measured by Tsuji *et al.*: they found that liquid Rb is compressed uniformly at 2.5 GPa, but that some deviation from uniform compression is observed at 6.1 GPa. In the present work, using the QHNC method in combination with the Rosenfeld bridge-functional for the reference hard-sphere system we have calculated the structure factors of compressed rubidium, the pressure ranging from 0 to 6.1 GPa and compared these data with the experimental results. We find excellent agreement with these experimental data, although in two cases the density has to be slightly readjusted. We confirm with our results the uniform compression model. We find out that the effective ion-ion potentials are insensitive to this pressure-variation, a feature which is obviously typical for liquid alkali metals (we also confirm these observations for the case of liquid-lithium). We finally observe that the structure factors coincide in one single curve if Q is scaled in units of the Wigner-Seitz radius a .

The paper is organized as follows: in the subsequent section we briefly outline the QHNC method and give a few details about the Rosenfeld bridge-functional. In Section III we discuss our results and compare them with experimental data. The paper is concluded by a

summary.

II. QHNC THEORY AND THE BRIDGE FUNCTIONAL

In the present section, we give a brief outline of the QHNC theory and the integration of the Rosenfeld bridge-functional in an integral equation approach for a one-component fluid.

Let us consider a liquid metal or a plasma as a mixture of electrons and ions interacting through pair potentials $v_{ij}(r)$ [$i, j = \text{e or I}$]. In this mixture, the ion-ion and electron-ion RDF's $g_{iI}(r)$ are identical with the ion- and electron-density distributions under the external potential caused by a fixed ion at the origin respectively, since the ions behave as a classical fluid in a liquid metal.² In general, DF theory enables us to provide exact expressions for the density distributions in an inhomogeneous system caused by an external potential. Hence, by applying DF theory to this mixture with densities n_0^i , we can derive exact expressions for the ion-ion and electron-ion RDF's in terms of direct correlation functions (DCF's) $C_{ij}(r)$ and bridge-functions $B_{iI}(r)$ as follows:²

$$g_{II}(r) = \exp[-\beta U_I^{\text{eff}}(r)] , \quad (2.1)$$

$$g_{eI}(r) = n_e^{0f}(r|U_e^{\text{eff}})/n_0^e , \quad (2.2)$$

with

$$U_i^{\text{eff}}(r) \equiv v_{iI}(r) - \frac{1}{\beta} \left[\sum_l \int C_{il}(|\mathbf{r} - \mathbf{r}'|) n_0^l [g_{II}(r) - 1] d\mathbf{r}' + B_{iI}(r) \right] \quad (2.3)$$

$$= v_{iI}(r) - \Gamma_{iI}(r)/\beta . \quad (2.4)$$

The wave equation for an electron under the external potential $U_e^{\text{eff}}(r)$ is solved to provide the total electron-density distribution $n_e(r)$ around a nucleus, which is divided into the bound-electron and free-electron parts: $n_e(r|U_e^{\text{eff}}) \equiv n_e^{0b}(r|U_e^{\text{eff}}) + n_e^{0f}(r|U_e^{\text{eff}})$ by the criterion whether their eigenfunctions belong to bound- or free-levels. In Eq. (2.2), the free-electron part of the density distribution, $n_e^{0f}(r|U_e^{\text{eff}})/n_0^e$, becomes identical to the electron-ion RDF; the bound-electron part $n_e^{0b}(r|U_e^{\text{eff}})$ is taken to form an ion and contributes to generate the

electron-ion interaction $v_{\text{el}}(r)$. These expressions for $g_{\text{el}}(r)$ can be rewritten in the form of a set of integral equations for a one-component fluid.² One of them is a usual integral equation for the DCF $C(r)$ of a one-component fluid:

$$C(r) = \exp[-\beta v_{\text{eff}}(r) + \gamma(r) + B_{\text{II}}(r)] - 1 - \gamma(r) , \quad (2.5)$$

with an interaction $v_{\text{eff}}(r)$ defined by

$$\beta v_{\text{eff}}(Q) \equiv \beta v_{\text{II}}(Q) - \frac{|C_{\text{el}}(Q)|^2 n_0^{\text{e}} \chi_Q^0}{1 - n_0^{\text{e}} C_{\text{ee}}(Q) \chi_Q^0} ; \quad (2.6)$$

the other is an equation for the effective interaction $v_{\text{eff}}(r)$, that is expressed in the form of an integral equation for the electron-ion DCF $C_{\text{el}}(r)$:

$$\hat{B}C_{\text{el}}(r) = n_{\text{e}}^{0f} (r | v_{\text{el}} - \Gamma_{\text{el}}/\beta - B_{\text{el}}/\beta) / n_0^{\text{e}} - 1 - \hat{B}\Gamma_{\text{el}}(r) . \quad (2.7)$$

In these equations, χ_Q^0 is the density response function of the noninteracting electrons with an electron density n_0^{e} and $\gamma(r) \equiv \int C(|\mathbf{r} - \mathbf{r}'|) n_0^{\text{I}} [g_{\text{II}}(r') - 1] d\mathbf{r}'$. Furthermore, \hat{B} denotes an operator defined by

$$\mathcal{F}_{\mathbf{Q}}[\hat{B}f(r)] \equiv \chi_Q^0 \int e^{i\mathbf{Q}\cdot\mathbf{r}} f(r) d\mathbf{r} . \quad (2.8)$$

It should be kept in mind that the electron-ion DCF in Eq. (2.6) plays the role of a nonlinear pseudopotential, which takes into account nonlinear electron-accumulations around an ion and the influence of other ions in the form of a linear-response expression; if the electron-ion DCF $C_{\text{el}}(r)$ is replaced by a usual pseudopotential $-\beta w_{\text{b}}(r)$, then $v_{\text{eff}}(Q)$ in Eq. (2.6) becomes an effective ion-ion interaction in pseudopotential theory based on the linear-response formalism.

From the above formal and exact expressions (2.5)-(2.7), the QHNC equations are obtained by introducing the following five approximations:²

1. The electron-ion bridge-function is neglected in Eq. (2.7): $B_{\text{el}} \simeq 0$ (the HNC approximation).

2. The bridge-function B_{II} of the ion-electron mixture is approximated by that of a one-component hard-sphere fluid (modified HNC – MHNC – approximation¹³).
3. The electron-electron DCF $C_{ee}(Q)$ in the ion-electron mixture is approximated by that of the jellium model: $C_{ee}(Q) \simeq -\beta v_{ee}(Q)[1 - G^{\text{jell}}(Q)]$, which is written in terms of the the local-field correction (LFC) $G^{\text{jell}}(Q)$. In our calculation we use the LFC proposed by Geldart and Vosko.¹⁴
4. An approximate $v_{eI}(r)$ is obtained by treating a liquid metal as a nucleus-electron mixture¹⁶ in the form:

$$v_{eI}(r) = -Z_A \frac{e^2}{r} + \int v_{ee}(|\mathbf{r} - \mathbf{r}'|) n_e^b(r') d\mathbf{r}' + \mu_{xc}[n_e^b(r) + n_0^e] - \mu_{xc}(n_0^e). \quad (2.9)$$

Here, $n_e^b(r)$ is the bound-electron distribution and $\mu_{xc}(n)$ the exchange-correlation potential in the local-density approximation, for which we have adopted the Gunnarsson-Lundqvist¹⁵ formula. Actually, the bound-electron distribution $n_e^b(r)$ is determined as the bound-electron part of $n_e(r|U_e^{\text{eff}}) \equiv n_e^{0b}(r|U_e^{\text{eff}}) + n_e^{0f}(r|U_e^{\text{eff}})$, when the electron-ion RDF in Eq. (2.7) is calculated from the wave equation for an electron under the external potential $U_e^{\text{eff}}(r) = v_{eI}(r) - \Gamma_{eI}(r)/\beta$.

5. The bare ion-ion interaction is taken as pure Coulombic: $v_{II}(r) = Z_I e^2/r$.

Under these approximations, a set of integral equations (2.5)-(2.7) can be solved; its solution allows the determination of the electron-ion and ion-ion correlations together with the ionization and the electron bound-states.

For the MHNC closure relation we have used in this work the parametrization for the bridge-function of a suitably chosen hard-sphere reference system that was proposed recently by Rosenfeld.⁸ In this version of the MHNC the universality hypothesis of the bridge-*function*¹³ (which 'justifies' the MHNC) is generalized to the level of the bridge-*functional* of the reference system. This functional can be calculated very easily for the general case of an inhomogeneous system of hard-spheres¹⁷ involving only fundamental measures; the

functional is then specialized – as required for our case – to a system of homogeneous hard-spheres. This fundamental measure bridge-functional is given in terms of characteristic quantities of the *individual* spheres and involves only integrations over known functions. Furthermore, in this approach the functional can be optimized by imposing the test-particle (or source-particle) self-consistency, which is realized by the transition from an inhomogeneous system to a homogeneous one if the source of the external potential becomes a particle of the liquid.²² The Ornstein-Zernike equation is then solved for the structure function of the homogeneous system along with the closure relation where the bridge-function is calculated by means of the above *functional*, assuming that the universality hypothesis is valid. The obtained structure function is then fed into the bridge-functional yielding a new, improved bridge-function. This procedure is iterated until numerical self-consistency is obtained in a sense that the structure function of the preceding step differs only marginally from the present step.

This method, which we denote by QHNC-MH, is in fact able to produce accurate data for the structure factors of Rb as demonstrated in Fig. 1 in the direct comparison with experiments¹⁸ at the triple point (313 K); the experimental data are denoted by the open and black circles.

III. RESULTS AND DISCUSSION

In this section, we apply the QHNC-MH method to calculate the structure factors for compressed liquid-rubidium under high pressure (0.2, 2.5, 3.9, and 6.1 GPa), i.e., exactly the same pressure-values under which Tsuji *et al.*¹⁰ performed their experiments to measure the structure factors. The corresponding densities are estimated by these authors to be 1.07, 1.41, 1.56 and 1.95 times the normal density; the temperatures are 370, 520, 540 and 570 K, respectively.

In a first step we apply our method to the 3.9 GPa state and examine how accurately the MHNC equation (in combination with the Rosenfeld bridge-function) is able to reproduce

the RDF obtained in an MD simulation: the comparison is shown in Fig. 2, where the QHNC-MH result (full curve) is found to be undistinguishable from the MD RDF (open circles). This comparison confirms that the QHNC-MH method is able to produce reliable structure-data that are as accurate as those obtained in computer-experiments even for compressed liquids at high densities; hence, MD simulations are no longer required in this study.

We can therefore proceed to compare the QHNC-MH results with *experimental* data for all high-pressure states: the structure factors calculated for pressures ranging from 0.2 to 6.1 GPa are plotted by full curves in Fig. 3 in comparison with the experimental results shown by full circles. We have found that our method gives structure factors in good agreement with experiment for 0.2 and 6.1 GPa. However, in the case of 2.5 and 3.9 GPa, the agreement between the theoretical and experimental results is not so convincing: a systematic deviation between the data sets is observed. In their analysis of their experiment, Tsuji *et al.*¹⁰ estimated the density of liquid Rb under pressure from the measured lattice constant of crystalline Rb including corrections for the thermal expansion and the volume jump at melting. However, according to Tsuji,¹⁹ there remains an uncertainty in the evaluation of the density, that might be responsible for these deviations. Therefore, we have modified the density for the 3.9 GPa case: when decreasing the ion-sphere radius (Wigner-Seitz radius) a [$a = (3V/4\pi)^{1/3}$ and V being the specific volume per ion] by a factor of 1/1.05 we can find indeed a good agreement between the theoretical and experimental results for the 3.9 GPa state, as shown in Fig. 4; a similar good agreement is found also for the 2.5 GPa case if the Wigner-Seitz radius a is decreased by 5 %.

It should be mentioned that the concept of our QHNC-method is for high pressures as reliable and valid as for the room pressure, since all the approximations entering this method remain valid as the pressure is increased. This fact can be seen from the result for the electronic structure, which will be discussed in the following. The bound levels of the ion in compressed liquid Rb are almost the same as those at room pressure. As a consequence, the electron-ion RDF's remain – as displayed in Fig. 5 – almost unchanged for

the five states considered. The electron-ion DCF $C_{eI}(r)$ is determined by Eq. (2.7). Figure 6 illustrates the pressure-variation of the electron-ion DCF $C_{eI}(r)$, which – as noted above – plays the role of a non-linear pseudopotential in the expression for the effective ion-ion interaction [cf. Eq. (2.5)]; also the electron-ion DCF does not change significantly under these pressure-variations.

Here, note that the electron-ion structure factor $S_{eI}(Q)$, the Fourier transform of the electron-ion RDF, is written in the following form:

$$S_{eI}(Q) = \sqrt{n_0^I n_0^e} C_{eI}(Q) \chi_Q^0 / D(Q) \quad (3.1)$$

$$= \frac{\rho(Q)}{\sqrt{Z_I}} S_{II}(Q), \quad (3.2)$$

where

$$\rho(Q) \equiv \frac{n_0^e C_{eI}(Q) \chi_Q^0}{1 - n_0^e C_{ee}(Q) \chi_Q^0}, \quad (3.3)$$

$$D(Q) \equiv [1 - n_0^I C_{II}(Q)][1 - n_0^e C_{ee}(Q) \chi_Q^0] - n_0^I n_0^e |C_{eI}(Q)|^2 \chi_Q^0. \quad (3.4)$$

Hence, Eq. (3.2) can be represented in r -space as

$$n_0^e g_{eI}(r) = \rho(r) + n_0^I \int \rho(|\mathbf{r} - \mathbf{r}'|) g_{II}(r') \mathbf{r}', \quad (3.5)$$

which states that the free-electron distribution $n_0^e g_{eI}(r)$ around an ion can be described exactly by the superposition of surrounding “neutral pseudoatoms”. Each ion carries a screening electron-cloud $\rho(r)$ [with $\int \rho(r) d\mathbf{r} = Z_I$], and makes it thus electrically neutral (including the core-electrons) as if it were an atom. Therefore, in this formalism a liquid metal can be considered to be composed by neutral pseudoatoms. Using Eq. (3.3), the free-electron density distribution of a pseudoatom is calculated for liquid Rb under high pressures (cf. Fig. 7): the results indicate that the electron-density distribution of a pseudoatom suffers no significant change outside of the core-region (where the bound-electron density is large) under this pressure-variation. Summarizing, we can conclude that a pseudoatom remains almost unchanged in comparison to room pressure even when the density is increased by a factor of nearly 2 (high pressure-state 6.1 GPa). On the other hand, Tsuji *et al.* expected

that a hard-sphere model²⁰ might be successfully applied to describe the structure of liquid alkali metals and that the effective diameter of the hard-sphere should vary with pressure due to the change in the screening effect; that is, the size of a pseudoatom is assumed to be changed with pressure. Based on this model, the effective hard-sphere radius σ_H is considered to vary under pressure-variation keeping the packing fraction $\eta = \pi n_0^I \sigma_H^3 / 6$ to be constant at a value of 0.45; this leads to a uniform-compression model in which the position of first peak Q_1 in the structure factor should increase proportionally to $(n_0^I)^{1/3}$ with increasing pressure.

We also find in our approach that the effective ion-ion interaction for liquid Rb is practically invariant under this pressure-variations (cf. Fig. 8), i.e., it remains almost the same as the one at room pressure. In contrast to the hard-sphere model, where the essential repulsive part of the effective ion-ion potential should be scaled in units of a , no scaling feature is observed for the effective ion-ion interaction in units of the Wigner-Seitz radius a . Nevertheless, all the structure factors for all these five pressure-values almost coincide in one single curve when scaling the wavenumber in units of the Wigner-Seitz radius a (as shown in Fig. 9).

Even if the liquid-rubidium potential under these pressure-variations can be considered as invariant with respect to the one at room pressure (neglecting small deviation), we have also observed the above mentioned scaling property in the structure factor (cf. Fig. 9); this means that the liquid-rubidium potential has a very special feature. For a *general* liquid (the Lennard-Jones potential for example), it is impossible to display the structure factor of two different states, scaled in length-units in such a way that they practically coincide. For a liquid alkali metal such a scaling property *can* be observed: to examine this, let us consider liquid Li as a further example. At first we calculate the effective ion-ion interaction of liquid Li at room pressure (470 K, n_0 with $r_s = 3.308$), and assume – as for Rb – that the effective Li potential is unchanged with respect to the one at room pressure. Then, we can easily find the following three sets of temperatures and densities: (470 K, n_0), (600 K, $1.34n_0$) and (750 K, $2.37n_0$), i.e. states for which the structure factors can be scaled almost in a single curve in unit of a , as demonstrated in Fig 10. For alkali liquid metals, this scaled structure factor

is not very sensitive to states specified by the plasma parameter $\Gamma \equiv \beta e^2/a$ and $r_s \equiv a/a_B$ in the sufficiently high-density region. This is the main reason why structure factors of all alkali liquids (from Li to Cs) near the triple point coincide almost in a single curve when scaling Q in units of the Wigner-Seitz radius a , as was observed experimentally^{23,24} and theoretically.^{25,7,26}

This scaling property in the structure factors of liquid Rb signifies that the first peak of the structure factor appears almost at the same position $Q_1 a$ (in scaled units) for all these pressures; this means that the position of the first peak Q_1 in the structure factor (taken in absolute values) should increase proportionally to $x = (V/V_0)^{-1/3}$, where V_0 is the specific volume at room pressure. In our calculation, this peak-position in reduced units is estimated from Fig. 9 to be $Q_1 a = 4.30$, from which we obtain the relation $Q_1 = 1.51x$ because of $a = r_s a_B = 2.58/x$; this linear relation is plotted in Fig. 11. In this figure, the full and the open circles denote the experimental points obtained for several states by Tsuji *et al.*,²¹ in particular, the five full circles represent those states which we have investigated in our theoretical study, i.e., for pressure-values 0, 0.2, 2.5, 3.9, and 6.1 GPa, respectively. These *experimental* Q_1 -points in Fig. 2.7 are close to the linear relation which was determined from the *calculated* structure factors; thus, this figure demonstrates that the uniform-compression model (corresponding to a linear relation denoted by the full line) is indeed valid, although there is some uncertainty due to difficulties in estimating the density and to problems in experiments under high pressure, in general.

IV. CONCLUSIVE DISCUSSION

The QHNC method in combination with the Rosenfeld bridge-functional has been shown to reproduce the experimental structure factors of liquid Rb under high pressures (ranging from 0 to 6.1 GPa) very accurately; for the case of 2.5 and 3.6 GPa the experimentally estimated densities have to be readjusted in terms of a 5 % variation of the Wigner Seitz radius a . Furthermore we observe that the structure factors coincide almost in one single

curve if wavenumber are scaled in units of a (Fig. 9). This indicates clearly that liquid Rb is uniformly compressed as the pressure is increased: this, in turn signifies, that the first peak-position Q_1 of the structure factors increases proportional to $(V/V_0)^{-1/3}$ (Fig. 11).

It must be mentioned that in contrast to our result, Shimojo *et al.*¹² conclude from their result obtained in the first-principles MD simulations that some deviation from uniform compression exists for the 6.1 GPa state, though liquid Rb is compressed uniformly at 2.5 GPa. Their experimental RDF's for 2.5 and 6.1 GPa are obtained by a Fourier transform of the experimental structure factors of Tsuji *et al.* On the basis of the RDF's they observe a different behaviour than on the basis of the structure factor, although they have used the same experimental structure factors and Rb states as we did: (i) the first-peak position in the RDF at 2.5 GPa follows the uniform compression model, while the first-peak position in the RDF at 6.1 GPa shows a deviation from the uniform compression model. Thus, they have asserted that their calculated result agrees with the experiment. (ii) In contrast to their RDF's, the experimental structure factor at 2.5 GPa shows a substantial deviation from the uniform compression compared to the 6.1 GPa state; the position Q_1 of the first peak in $S_{II}(Q)$ lies far away from the uniform compression line in Fig. 11 while on the other hand, the experimental structure factor at 6.1 GPa shows that the uniform compression model is still valid: the Q_1 -point for 6.1 GP in Fig. 11 is very close to the uniform compression line.

According to Tsuji,¹⁹ this discrepancy between the conclusions based on the RDF's and the structure factors is possible, since there is some experimental ambiguity in the value of the peak height in the structure factor while the peak-position is accurate and reliable. Nevertheless, from all the experimental data displayed in Fig. 11, we can conclude that liquid Rb is compressed uniformly up to a pressure of 6.1 GPa; however, a more detailed discussion if deviations from the uniform compression model (cf. Fig. 11) have any physical meaning is not very conclusive, due to the uncertainty in the evaluation of the experimental density and the difficulties encountered in experiments under high pressure.

It is interesting to notice that the structure factors of compressed liquid Rb coincide practically in one single curve if wavenumbers are scaled in units of the Wigner-Seitz radius

a , despite of the fact that the effective ion-ion interaction remains under pressure unchanged with respect to room pressure; this means that interaction potentials of liquid alkali metals have a special characteristic property, as we have demonstrated and confirmed in addition for the case of liquid Li in Fig. 10. The neutral pseudoatom in compressed liquid Rb remains almost unchanged under pressure-variation, which, in turn, is the reason why the effective ion-ion interaction remains practically invariant, similar to state-*independent* interactions, such as the one for liquid argon.

We have demonstrated in this contribution that the QHNC method can treat the 'outer-structure' problem (i.e., calculation of the ion-ion and electron-ion RDF's) and the 'inner-structure' problem (i.e., calculation of the electronic structure of the ion) in a self-consistent way using the atomic number as the only input data: therefore, this method can be considered to be very useful to treat a plasma, where the ionization Z_I is not known beforehand and where there is no way of constructing a pseudopotential to give the effective ion-ion interaction. From the successful results for compressed liquid Rb presented here we can conclude that the QHNC method is expected to be nicely applicable for plasma states in a wide range of densities and temperatures.

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FIGURES

FIG. 1. Ion-ion structure factor $S_{II}(Q)$ for liquid Rb at a temperature of 313 K; the QHNC-MH method (in combination with the the Rosenfeld bridge-functional) yields a structure factor (full curve) in excellent agreement with experiments¹⁸ (open and full circles).

FIG. 2. Ion-ion RDF $g_{II}(r)$ at a pressure of 3.9 GPa (full curve) calculated by the QHNC-MH method: results are undistinguishable from those obtained in MD simulations (open circles).

FIG. 3. Structure factors $S_{II}(Q)$ of liquid Rb under high pressures: 0.2, 2.5, 3.9 and 6.1 GPa; the QHNC-MH results (full curve) are compared with experiment¹⁰ (full circles). The densities corresponding to these pressures are 1.07, 1.41, 1.56 and 1.95 times the normal density n_0 , respectively.

FIG. 4. The reestimated structure factor $S_{II}(Q)$ (full curve) of liquid Rb at 3.9 GPa where the Wigner-Seitz radius a has been decreased by a factor of 1/1.05 as a unit of length; excellent agreement with experimental results¹⁰ (open circles) is observed

FIG. 5. The electron-ion RDF's $g_{eI}(r)$ of liquid Rb under pressure (ranging from 0 to 6.1 GPa); note that the g_{eI} 's remain almost unchanged under pressure-variation.

FIG. 6. The electron-ion DCF's $C_{eI}(r)$ of liquid Rb under pressure (ranging from 0 to 6.1 GPa); these functions play the role of a nonlinear pseudopotential $w_b(r)$ to determine the effective ion-ion interaction.

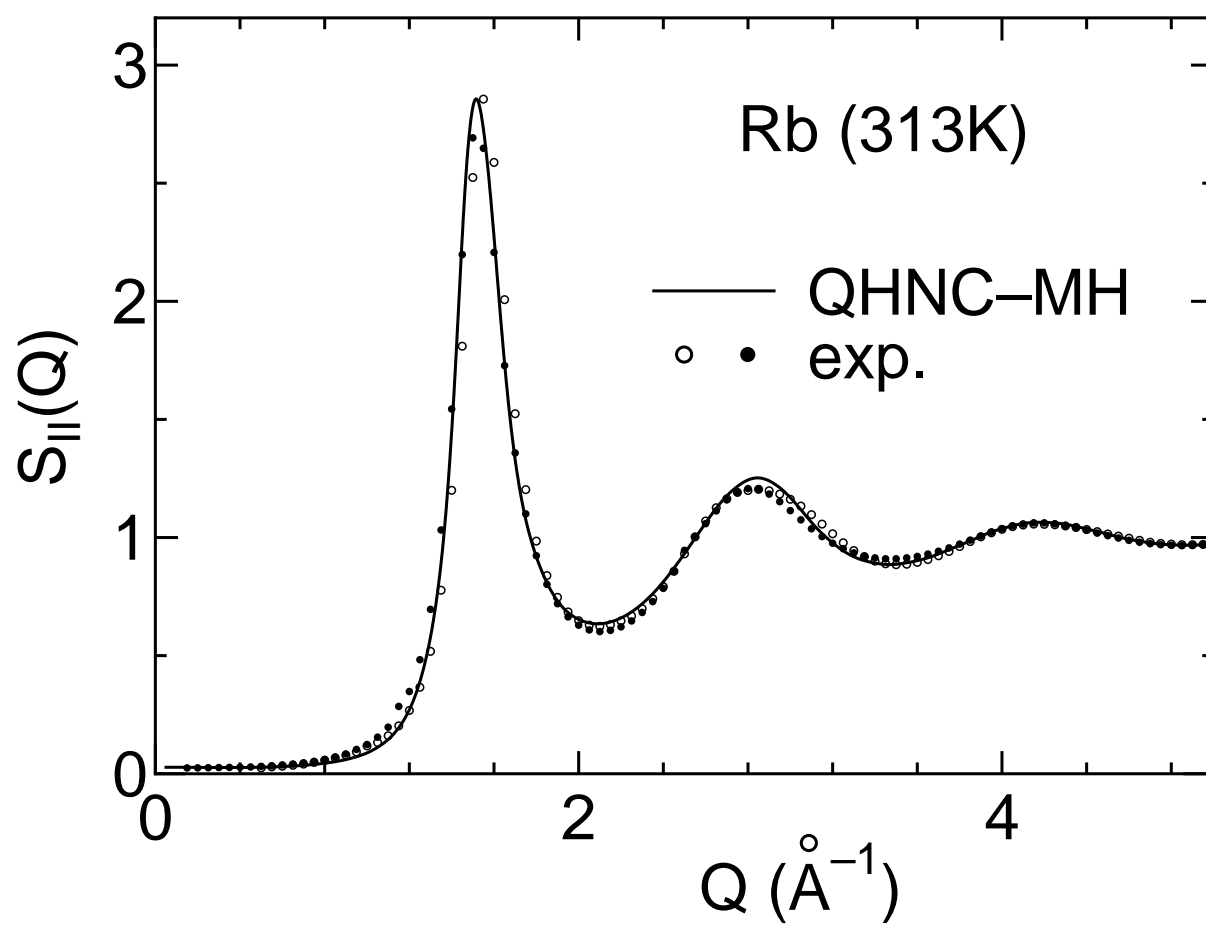
FIG. 7. The electron-density distribution $\rho(r)$ of a pseudoatom in liquid Rb under pressure (ranging from 0 to 6.1 GPa); the 5s-electron density distribution of a free atom is displayed for comparison (small full circles). $\rho(r)$ is plotted in units of a_B^{-3} (a_B being the Bohr radius).

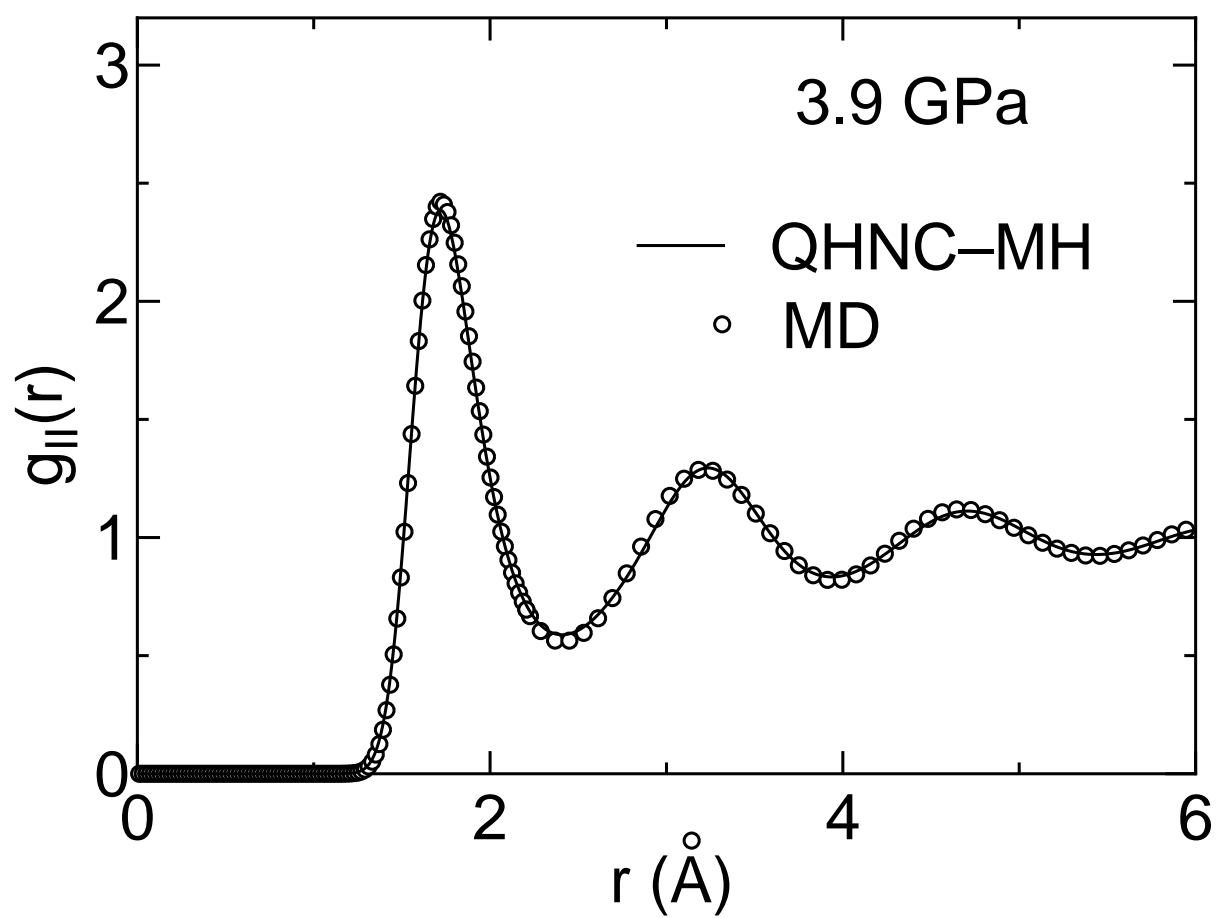
FIG. 8. The effective ion-ion interaction $v_{\text{eff}}(r)$ of liquid Rb under pressure (ranging from 0 to 6.1 GPa); the effective interaction for compressed liquid Rb remains practically unchanged with respect to room pressure.

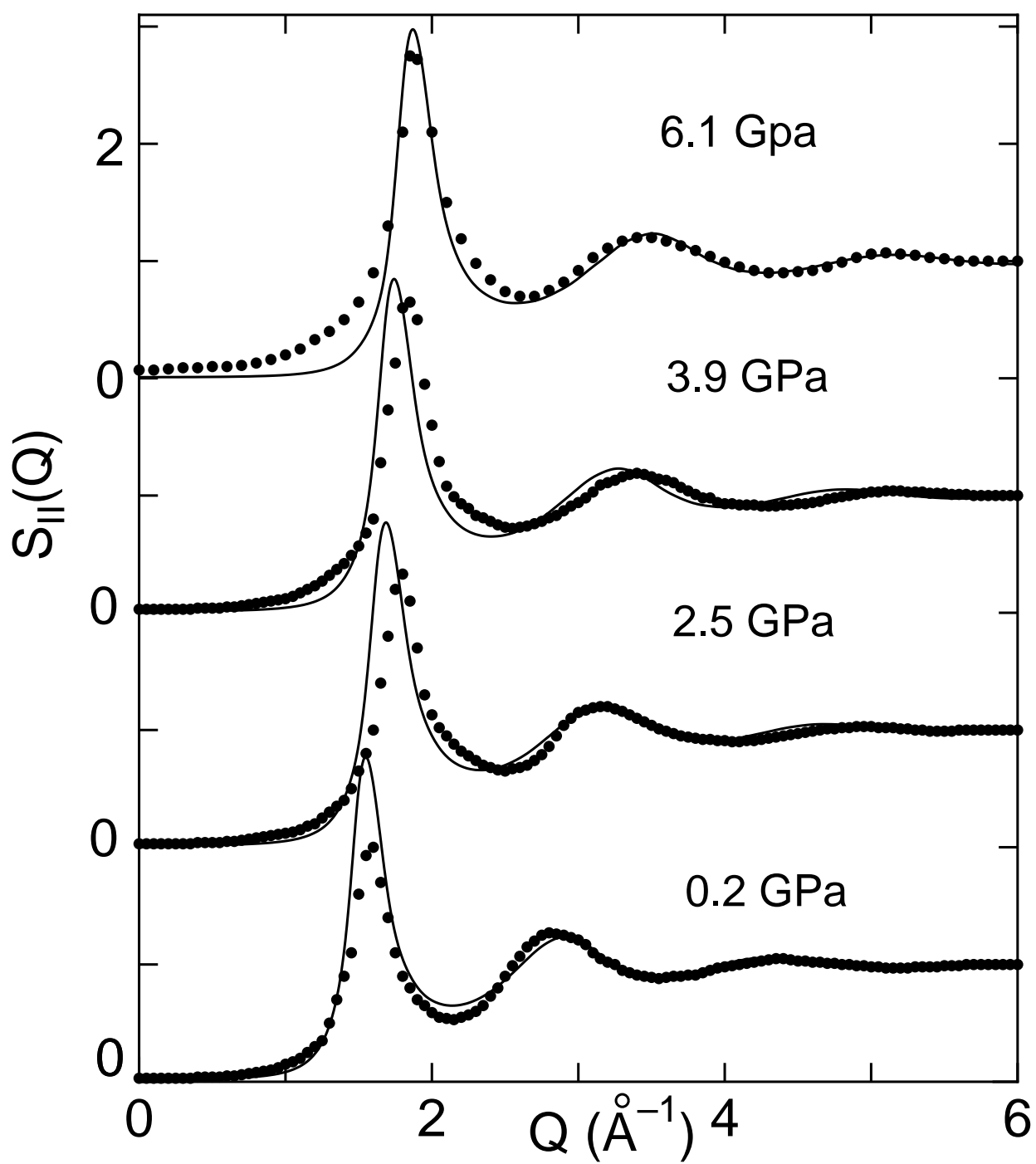
FIG. 9. Structure factors $S_{\text{II}}(Q)$ of liquid Rb calculated for 0, 0.2, 2.5, 3.9, and 6.1 GPa; all results are scaled in units of the Wigner-Seitz radius a and practically coincide in one curve; the experimental result¹⁰ for 6.1 GPa is plotted by full circles.

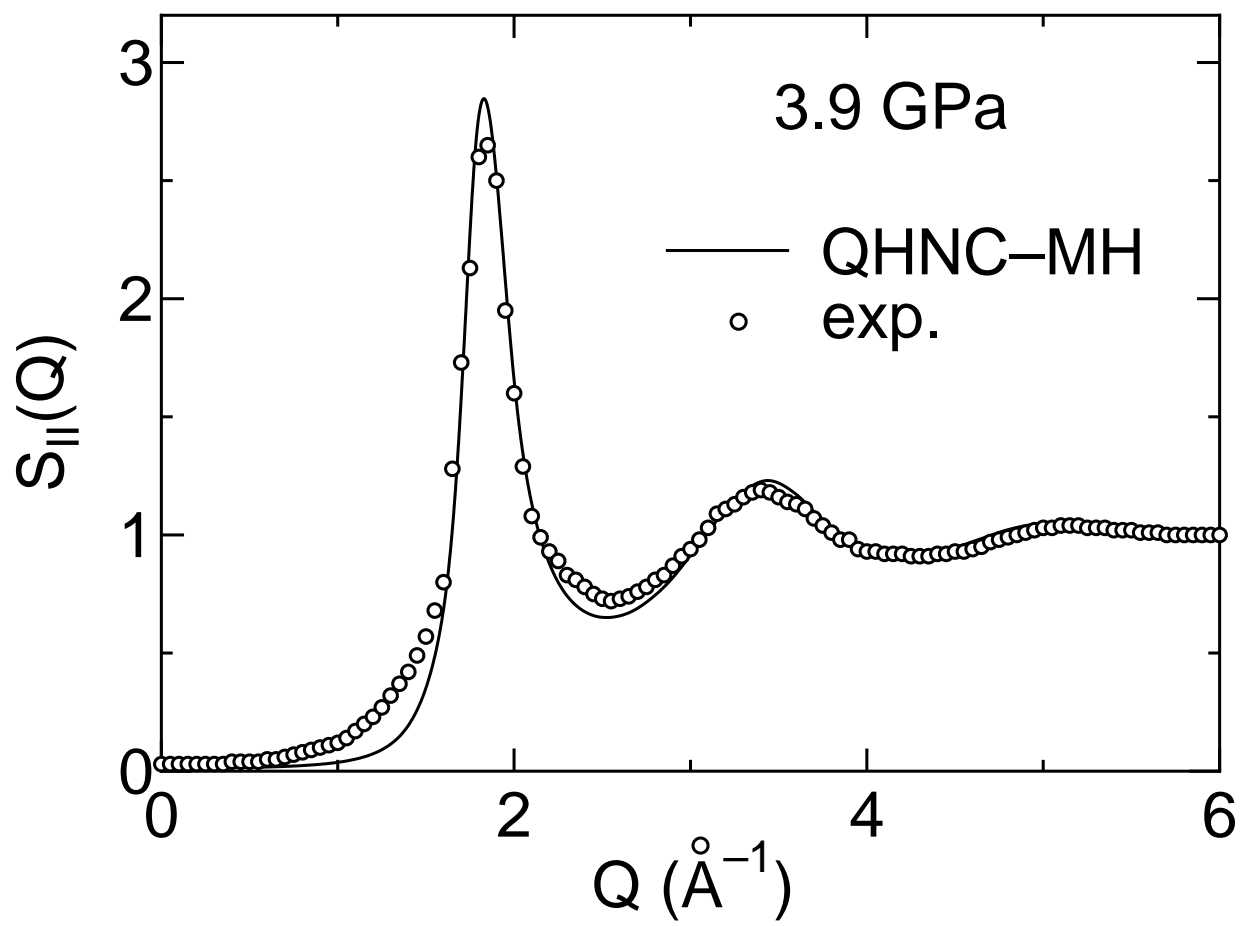
FIG. 10. Structure factors $S_{\text{II}}(Q)$ of liquid Li calculated for two states, $(1.34n_0, 600 \text{ K})$ and $(2.34n_0, 750 \text{ K})$ under the assumption that the effective ion-ion interaction is the same as that for room pressure. The structure factor (full curve) of liquid Li at room pressure is also plotted for comparison; when scaled in units of the Wigner-Seitz radius a , all three structure factors practically coincide in a single curve.

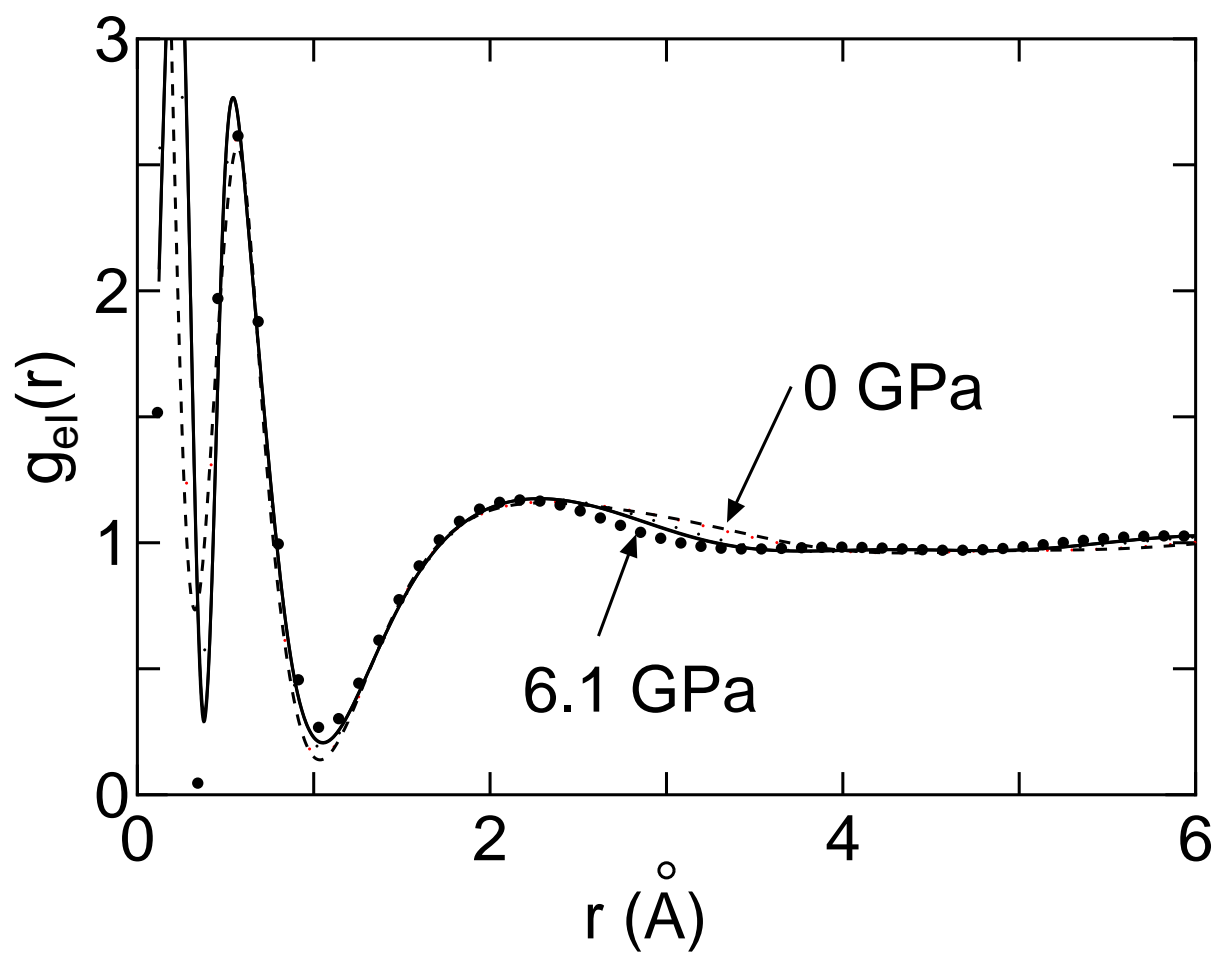
FIG. 11. The position of the first peak Q_1 in the structure factor for liquid Rb as a function of $(V/V_0)^{-1/3}$; open and full circles represent experimental results.²¹ In particular, the full circles are the points determined from the experimental structure factors under pressure: 0, 0.2, 2.5, 3.9, and 6.1 GPa plotted in Figs. 1 and 3. The solid line denotes our calculated results (uniform compression model) derived from the first peak-position ($Q_1 a = 4.30$) in the scaled structure factor in Fig. 9.

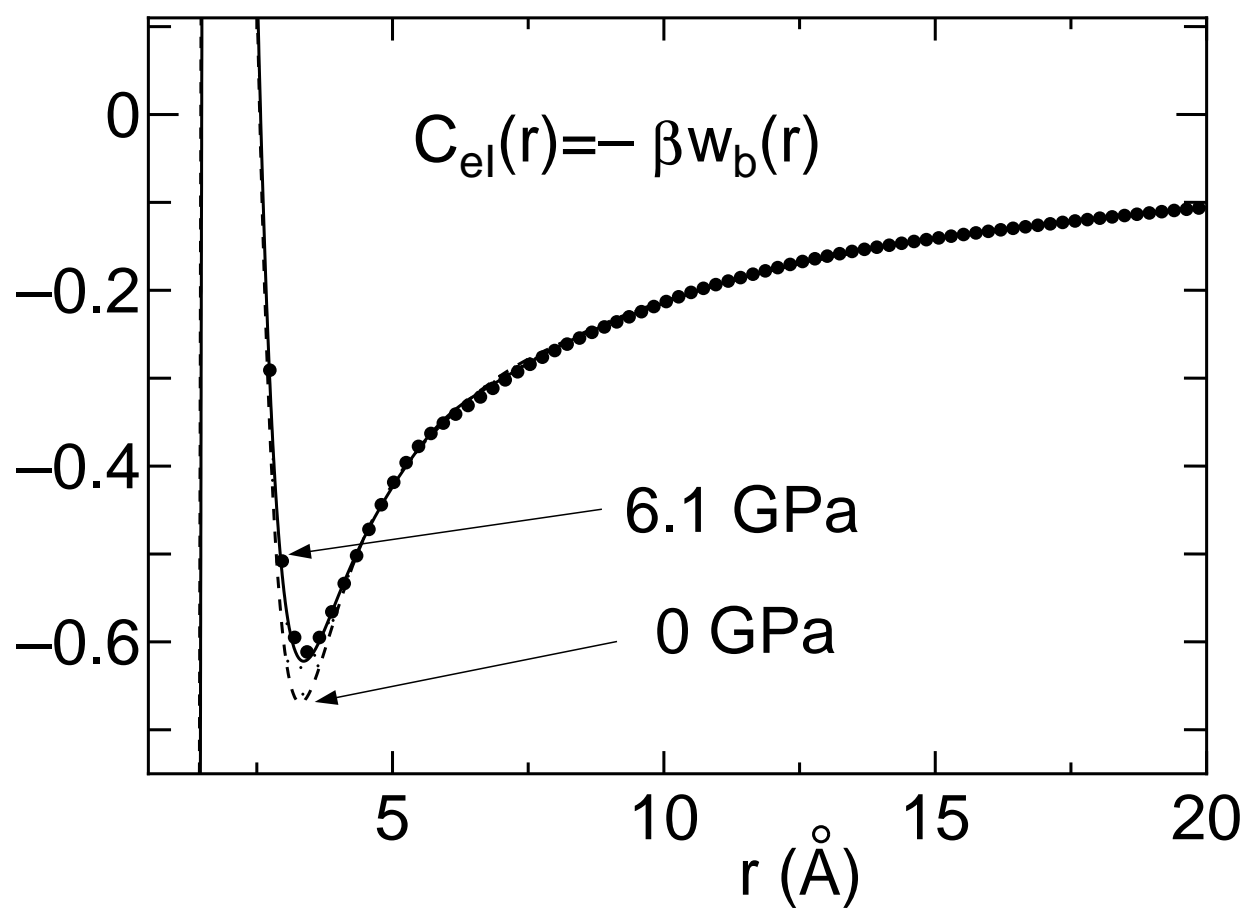












$[1 \times 10^{-3}]$

